of composition corresponding to that of the isothermally invariant point even at this temperature, and that crystallization would result in the separation of both phthalic acid and sodium acid phthalate, rendering the product useless as a volumetric standard. An impurity of sodium phthalate, on the other hand, will do no harm to the final product as the composition of the solution will move to the left and away from this isothermally invariant point. It is for this reason that an amount of sodium carbonate slightly in excess of the calculated quantity is used in the preparation of sodium acid phthalate.

Summary

1. The solubility relations in the ternary system, sodium phthalate, phthalic acid and water at 0, 25, 35 and 50° have been determined.
2. Double salt formation has been found to take place at all of these temperatures.
3. The composition of this double salt has been shown to be $2NaHC_8H_4O_4 \cdot H_2O$.
4. It has been pointed out that sodium acid phthalate should be recrystallized from aqueous solution at temperatures not lower than 50°.
5. It is recommended that in the preparation of sodium acid phthalate for use as a volumetric standard an amount of alkali be used which is slightly in excess of the calculated quantity.

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RECEIVED JANUARY 27, 1933
PUBLISHED JUNE 6, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Interfacial Tension of Mercury in Contact with Organic Liquids

BY F. E. BARTELL, LEE O. CASE AND HENRY BROWN[1]

A study of the literature shows comparatively great discrepancies in the recorded values for the interfacial tension of mercury against different liquids, but fails to disclose the cause of these discrepancies. Impurities present in the materials used or difference in methods employed might account for the variations observed. Harkins and Grafton[1a] using the drop weight method obtained a value of 375 dynes/cm. for water against mercury, while Burdon and Oliphant[2] using the sessile drop method obtained a value of 427 dynes/cm. for the same system. It will be noted that the first mentioned method is a dynamic method; the second a static method.

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(1) The material presented in this paper is from a portion of a dissertation submitted by H. Brown to the graduate school of the University of Michigan, in partial fulfilment of the degree of Doctor of Philosophy, 1932.

(1a) Harkins and Grafton, THIS JOURNAL, **42**, 2534 (1920).

(2) Burdon and Oliphant, *Trans. Faraday Soc.*, **23**, 205 (1927).

Inasmuch as we were in immediate need of the most accurate interfacial tension data obtainable, it was decided to carry out a series of measurements making use of both a dynamic method and a static method so that their degree of accuracy might be compared. Accordingly, the drop weight method and the capillary rise method were adopted for use. As our work progressed it was found that the values obtained by these two methods showed comparatively good agreement throughout. Some of the values obtained were not, however, in close agreement with generally accepted values in the literature. A brief description of methods and some of the results obtained follow.

Apparatus and Experimental Procedure

Drop Weight Method.—A sketch of the drop weight apparatus used is given in Fig. 1. In this apparatus, a modification of that of Harkins,[3] the dropping tip was made of Pyrex tubing and was selected after examining for circularity many feet of tubing of inner diameter 1.4 to 1.2 mm. (the size used by Harkins and co-workers). In cutting the pieces of tubing a sharp scratch was made with a tungsten edged knife and on pulling the tubing apart at the scratch mark it was found that in many cases the break left a plane surface with an exceedingly sharp edged inner bore normal to the length of the tube. This is the most desirable kind of tip for use with mercury. The diameter of the inner bore of the tip used was 1.242 ± 0.001 mm. (measured with a comparator along eight different diameters).

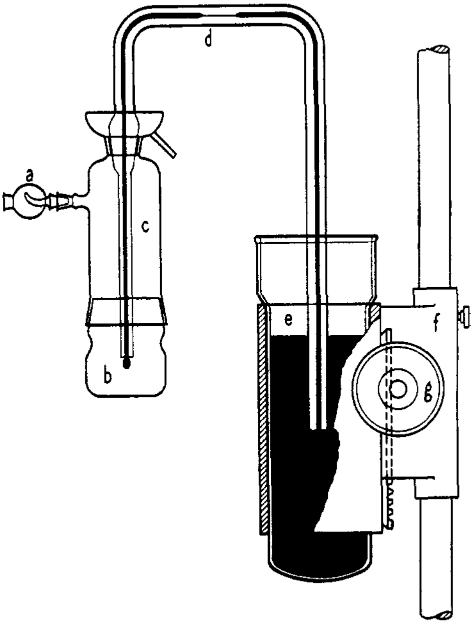

Fig. 1.—Drop weight method for mercury against liquids and saturated vapors.

The dropping tip was sealed to a tube which had a very fine constriction as indicated in the figure. With this fine constriction and with the ratchet and pinion device to alter the head of the mercury in the reservoir, the rate of fall of the drops could be suitably controlled. The tube *d* was held firmly in place on a stable support. This support was separate from the one carrying the reservoir of mercury *e* in order that no vibrations caused by operating the ratchet and pinion would be communicated to the hanging drop. The jacket *c* was connected to the tubing *d* by means of a ground glass joint (it was found unnecessary to use the mercury seal on this joint). Six cups of type *b* were ground to fit jacket *c*. The apparatus was placed in a large air thermostat (120 × 130 × 80 cm.) which kept the temperature constant to ±0.05°.

The determinations were carried out in the following manner. Enough pure liquid was distilled directly into cups *b*, which had been previously cleaned, steamed and dried,

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(3) Harkins and Brown, This Journal, **41**, 499 (1919).

so that when the cups were placed in position the liquid covered the dropping tip (about 10 cc. of liquid in each cup). The cups were then covered with ground-glass plates and allowed to stand for about one hour in the thermostat before measurements were started. Usually 7 or 8 drops of mercury were collected in each cup. The drops were allowed to form in the course of about three minutes, and then by lowering the mercury head they were allowed to detach in the course of about two minutes. In placing the cups in position for the measurements it is essential that no air bubbles be trapped against the tip as these may cling to the drop and thus invalidate the correction for buoyancy of the mercury drop.

After the drops had been collected, most of the lighter liquid used was drawn off from the mercury by means of suction applied to a small pipet. This pipet was provided with a trap, and was similar in construction to a Drechsel test-tube. The mercury was next covered with acetone and the acetone solution was then drawn off. Finally the cup with the mercury was placed near a fan to evaporate all the acetone. In about fifteen minutes the mercury was ready for weighing.

In none of the measurements were erratic results obtained. This was doubtless due to the razor-edged sharpness of the inner bore of the tip used, as well as to the bulging form of the drop, and to the very high degree of purity of all of the liquids used. It was found that in nearly every case the measurements could be duplicated to within about 0.3%.

Capillary Rise Method.—A diagrammatic sketch of the capillary rise (or capillary depression) apparatus[4] used is shown in Fig. 2. The entire apparatus was of Pyrex glass. The internal diameters of the cups *M* and *N* were 4 cm. In making a measurement the following procedure was observed.

Mercury was drawn from a reservoir and allowed to flow through capillary glass tubing directly into cup *M* while the three-way stopcock was closed at *O*. When there was sufficient mercury in cup *M* the stopcock was turned so that some mercury flowed out at *P*, then by making communication to the capillary by means of the stopcock a fresh surface of mercury could be caused to enter the capillary *Q*. Before the mercury was allowed to flow into the capillary, the second liquid was put into cup *N* and by turning the stopcock the first portion of the liquid (organic liquid or water) was allowed to flow out at *P*. The stopcock was then turned so that the mercury would rise slowly into the capillary. Since the capillary had already been wetted by organic liquid, or water, it was believed that a stable film had been formed on the wall and that the interfacial contact angle formed between the mercury and this film would be a zero angle. The values obtained with this apparatus are given in Table II.

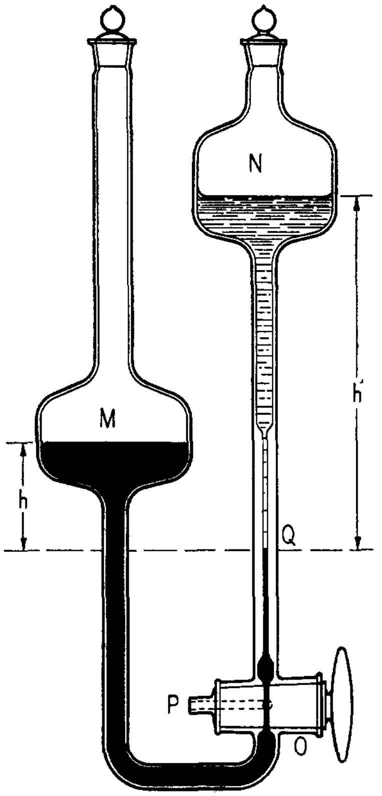

Fig. 2.—Capillary rise method for interfacial tensions of mercury against liquids.

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(4) *Cf.* Bartell and Miller, This Journal, 50, 1961 (1928).

Purification of Liquids

The liquids used were liquids for which the physical constants had already been accurately determined and the method of preparation in a pure state carefully studied.[5]

Alcohols.—The alcohols used were refined alcohols and were further treated by distillation from a small amount of potassium hydroxide and silver nitrate to remove traces of aldehydes. They were then dehydrated with quicklime and distilled from the lime, and finally made anhydrous by the use of metallic magnesium and iodine according to the method of Lund and Bjerrum.[6]

***n*-Hexane.**—The synthetic hexane of Eastman Kodak Company was used. It was further purified by washing repeatedly with concentrated sulfuric acid, then with alkaline permanganate, then with water, was refluxed with mercury, then dried with fused potassium hydroxide, then with sodium and finally distilled twice from fresh sodium.

***n*-Heptane.**—The *n*-heptane was obtained from the Research Laboratories of the Ethyl Gasoline Corporation It was of high purity and received no further chemical purification except that it was distilled from sodium before use.

Benzene.—Thiophene-free benzene was stirred for three days with concentrated sulfuric acid using fresh acid each day. It was then washed twice with water, then with sodium hydroxide solution, next dried with fused calcium chloride and then fractionally distilled from phosphorus pentoxide. Finally it was fractionally crystallized eight times when the crystals were perfectly transparent and of a very large size. It was distilled from phosphorus pentoxide before use.

Toluene.—This was synthesized from *p*-bromotoluene by means of the Grignard reaction and then the Grignard compound was hydrolyzed with hydrochloric acid in ice water. The toluene layer was separated, dried with calcium chloride, refluxed with sodium and then fractionally distilled three times from sodium.

***n*-Propylbenzene and *n*-Butylbenzene.**—The *n*-propylbenzene and *n*-butylbenzene were synthetic products previously prepared in this Laboratory.[7] Owing to their high purity they were merely refluxed with sodium before distillation from fresh sodium to ensure the removal of any traces of halogen compounds.

Nitrobenzene.—A C. P. grade of nitrobenzene was washed with dilute hydrochloric acid to remove basic impurities, and it was then allowed to stand over potassium carbonate. It was next steam distilled and dried over potassium carbonate. Finally it was fractionally distilled twice, and fractionally crystallized twice.

Water.—Ordinary distilled water was distilled from alkaline permanganate through a block tin condenser. It was then redistilled from quartz.

Mercury.—Redistilled mercury was repeatedly shaken with dilute nitric acid to a gray mercury emulsion and then washed thoroughly with water; next it was dried and filtered through a hard filter with a pin point opening. It was then redistilled twice in a current of air at low pressures according to the method of Hulett.[8]

The densities and boiling points of all liquids checked closely with the critical values given by Timmermans and Martin. The freezing point was taken only for benzene and was 5.51 ± 0.02°, which checks with the best values for this constant.

Results and Discussion

In Table I are given the interfacial tension values obtained by the drop weight method for mercury in contact with each of twelve pure liquids which are without chemical action on the mercury. For water, nitro-

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(5) Timmermans and Martin, *J. chim. phys.*, **23**, 733 (1926); **25**, 411 (1928).

(6) Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

(7) They were prepared by G. L. Mack by means of the Wurtz–Fittig reaction and also purified by him. Acknowledgment is gratefully made to him for the use of these liquids.

(8) Hulett, *Phys. Rev.*, **33**, 307 (1911).

benzene and hexane against mercury, the results show close agreement with accepted values. In the other cases in which values were available for comparison the deviations ranged from 4 to 13 dynes per cm.[9].

TABLE I

INTERFACIAL TENSION OF MERCURY AGAINST VARIOUS LIQUIDS AT 25° BY THE DROP WEIGHT METHOD

Liquid	Density	(*M*) Uncorrected drop weight, g.	(*m*) g.	$f\left(\frac{r}{v^{1/3}}\right)$	Interfacial tension dynes/cm., calcd.	From literature[a] (20°)
Water	0.9970	0.1163	0.0086	0.7240	374.1	375
Ethyl alcohol	.7850	.1151	.0067	.7235	376.9	364
n-Propyl alcohol	.7993	.1152	.0068	.7235	376.5	368
n-Butyl alcohol	.8058	.1141	.0068	.7231	372.8	...
Isoamyl alcohol	.8125	.1145	.0069	.7232	373.7	261.3
Hexane	.6570	.1150	.0056	.7235	379.9	378
Heptane	.6794	.1147	.0058	.7233	378.7	...
Benzene	.8736	.1119	.0072	.7222	364.3	351.2
Toluene	.8622	.1113	.0070	.7218	363.6	359
n-Propylbenzene	.8574	.1113	.0070	.7218	363.1	...
n-Butylbenzene	.8561	.1111	.0070	.7217	362.5	...
Nitrobenzene	1.1980	.1100	.0097	.7212	349.5	350.5

[a] "International Critical Tables," Vol. IV, p. 438.

A study of the interfacial tension values with mercury is interesting because, unlike most liquid–liquid systems, the mutual solubility is negligibly small. This absence of solubility makes possible the accurate calculation of the work of adhesion between mercury and other liquids without involving solubility effects.

On the basis of the data now available, a comparison of the interfacial tension relationships can be made between liquid–liquid systems in which the mutual solubility is appreciable and those in which it is negligible.

First, in the case of slightly miscible systems as those of most organic liquids with water, it is well known that if in an homologous series of such organic liquids against water, the mutual solubility decreases as the series is ascended, the interfacial tension between the co-existing phases will be found to increase in this series. Thus in this case the interfacial tension and the surface tension of the organic liquid vary in the same direction in the series.

Second, in the case of systems in which the mutual solubility is so small as to be considered negligible, very little difference in interfacial tension values in the homologous series is noted. Examples of such behavior are furnished by the systems mercury with organic liquids, and water with the paraffin hydrocarbons such as hexane and octane (see Tables III and IV). It is believed worth while, however, to point out that the values in the tables do show a slight regular difference in each homologous series against mercury and also for the paraffin hydrocarbons against water, and, if this difference is real, it must be due to effects other than those attributable to

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[9] Harkins, "International Critical Tables," Vol. IV, p. 438.

TABLE II

INTERFACIAL TENSION OF MERCURY AGAINST VARIOUS LIQUIDS AT 25° BY THE CAPILLARY RISE METHOD

d_{Hg} = 13.534 g./cc. r = 0.03201 cm.

Liquid	Density	h', cm.	h	Meniscus correction $1/3r(d - d')$	Interfacial tension, dynes/cm.
Hexane	0.6570	14.070	2.455	0.137	378
Benzene	.8736	14.170	2.600	.135	361
Water	.9970	15.070	2.870	.133	375
Nitrobenzene	1.1980	14.350	2.910	.131	350

r = radius of capillary
d = density of mercury
d' = density of lighter liquid
h = height of lighter liquid surface above meniscus
h' = height of mercury surface above meniscus (see Fig. 2)

TABLE III

INTERFACIAL TENSION VALUES OF DIFFERENT MEMBERS OF AN HOMOLOGOUS SERIES OF ORGANIC LIQUIDS AGAINST MERCURY, OBTAINED WITH DROP WEIGHT METHOD

Liquid	Interfacial tension against mercury at 25°	Liquid	Interfacial tension against mercury at 25°
Ethyl alcohol	376.9	Benzene	364.3
n-Propyl alcohol	376.5	Toluene	363.6
n-Butyl alcohol	372.8	*n*-Propylbenzene	363.1
Isoamyl alcohol	373.7	*n*-Butylbenzene	362.5

TABLE IV

INTERFACIAL TENSION VALUES OF DIFFERENT MEMBERS OF AN HOMOLOGOUS SERIES OF ORGANIC LIQUIDS AGAINST MERCURY AND AGAINST WATER, OBTAINED WITH DROP WEIGHT METHOD

Liquid	Interfacial tension against mercury at 25°	Interfacial tension against water at 20°
n-Hexane	379.9	51.1 ± 0.2
n-Heptane	378.7	....
n-Octane	376.0	50.81 ± 0.1

mutual solubility. Further, the order of decreasing interfacial tension values is, in every case, the same as the order of increasing surface tension values of the organic liquids in the homologous series. Considering the interfacial tension values to be dependent upon the difference between the surface tensions of the two phases in equilibrium with each other, we may conclude that *in absence of solubility*, the interfacial tension values for the members of an homologous series against a given liquid will decrease progressively if the surface tension values of the organic liquids increase progressively in the series. It will be noted that this relationship is just opposite to the one which obtains for systems in which the mutual solubility is appreciable.

The Interfacial Tension of Mercury in Contact with Organic Halogen Compounds.—In addition to the data given in the preceding tables, interfacial tension measurements were made with the liquids chlorobenzene, bromobenzene, ethylene chloride and ethylene bromide. Although these measurements were carefully made, the results are not included in Table II in the belief that they may not be as reliable as those recorded, due to the impossibility of avoiding chemical reaction of these liquids with mercury.

That these liquids as ordinarily prepared and used tend to give erroneous values is clearly shown by our measurements with ethylene bromide. For the interfacial tension of mercury against a sample of ethylene bromide which had been purified by the usual chemical methods and then distilled a value was obtained which was in agreement with that obtained by Harkins and Grafton for this system. The ethylene bromide was then subjected to further purification. It was agitated with mercury for six hours (the mercury surface remained bright), ten times fractionally crystallized, and finally distilled under nitrogen at low pressures (to minimize any danger of the liberation of free bromine by displacement by oxygen of the air). When the interfacial tension was measured with this new sample, a value of 346 dynes/cm. at 25° was obtained—20 dynes higher than the previous value.

It is seen that deductions made from interfacial tension measurements of mercury against even the most carefully purified halogen or sulfur compound may be untrustworthy. The value may not represent the true free surface energy value between mercury and the compound, but instead may represent the free surface energy relation between mercury and a very dilute solution consisting of capillary active impurities and the otherwise pure liquid. This would apply in the case of organic compounds of iodine and sulfur and probably to most organic compounds of bromine, especially aliphatic bromides. The instability or reactivity (with oxygen and moisture as well as with metals themselves) of organic halogen compounds (especially saturated aliphatic bromides and iodides) and sulfides is common knowledge, and therefore the danger of formation of capillary active impurities (mercury salts of the halogens or sulfur) is always present. We have obtained values for some carefully purified organic halogen compounds which we believe are not far from the true values; for chlorobenzene, the interfacial tension obtained against mercury was 353 dynes per cm., for bromobenzene 347 and for ethylene chloride 358, all at 25°. The work with organic compounds of halogens would indicate that the specific effects (*i. e.*, attraction of the halogen radicals toward the mercury atoms) are not as strong as has previously been believed.[10]

Summary

1. Measurement of interfacial tension of pure liquids against mercury with both the drop weight method and the capillary rise method gave results showing close agreement, indicating that either the dynamic method

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[10] Harkins and Grafton, THIS JOURNAL, **42**, 2534 (1920); Harkins and Ewing, *ibid.*, **42**, 2539 (1920).

or the static method is suitable for such measurements. Some of the results obtained did not show close agreement with generally accepted values in the literature.

2. Interfacial tension values were obtained for certain halogen derivatives against mercury. These values are higher than those previously recorded.

3. Interfacial tension values were obtained for some liquids against mercury for which no data are given in the literature.

4. Data obtained for an homologous series of organic liquids against mercury indicated that, in the absence of solubility effects, the interfacial tension values of the members of an homologous series against a given liquid will decrease progressively if the surface tension values of the organic liquids increase progressively in the series.

ANN ARBOR, MICHIGAN

RECEIVED JANUARY 30, 1933
PUBLISHED JUNE 6, 1933

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 28]

The Free Energy of Reactions Involving the Fused Chlorides and Bromides of Lead, Zinc and Silver

BY EDWARD J. SALSTROM

In the course of a series of studies on the thermodynamics of fused salt solutions, the free energy of formation of fused lead bromide,[1a] silver bromide,[1b] lead chloride[2] and zinc chloride,[2] calculated from the e. m. f. measurements on cells of the type, Pb(liq.), $PbBr_2$(liq.), Br_2(g), have already been given. With the aid of these data and measurements of the e. m. f. values of the cells Ag(s), AgCl(l), Cl_2(g) and Zn(l), $ZnBr_2$(l), Br_2(g) herein presented, the free energies of a series of chemical reactions have been calculated.

The apparatus and part of the experimental procedure were essentially the same as those previously described.[1a] Features peculiar to this research are briefly as follows. The silver chloride, containing a maximum impurity content of 0.014%, was obtained from commercial sources and used without further purification except for drying as described below. The zinc used as the negative electrode and the lead chloride serving as a source of chlorine were also from commercial sources of highest purity. The zinc bromide used in the cell and the lead bromide used as a source of electrolytic bromine were prepared as recently described.[3]

The chlorine gas used as an electrode in the cell (Ag(s), AgCl(l), Cl_2(g) was obtained by electrolyzing fused lead chloride which had been freed

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(1) (a) Salstrom and Hildebrand, THIS JOURNAL, **52**, 4641 (1930); (b) *ibid.*, **52**, 4650 (1930).

(2) Wachter and Hildebrand, *ibid.*, **52**, 4655 (1930).

(3) Salstrom, *ibid.*, **55**, 1029 (1933).